

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number:

**0 487 273 B1**

(12)

**EUROPEAN PATENT SPECIFICATION**(45) Date of publication of patent specification: **14.06.95** (51) Int. Cl.<sup>6</sup>: **C23C 4/04, F01D 11/08**(21) Application number: **91310594.6**(22) Date of filing: **15.11.91**(54) **Thermal spray powder.**(30) Priority: **19.11.90 US 615557**(43) Date of publication of application:  
**27.05.92 Bulletin 92/22**(45) Publication of the grant of the patent:  
**14.06.95 Bulletin 95/24**(84) Designated Contracting States:  
**CH DE ES FR GB IT LI**(56) References cited:  
**DE-A- 2 413 382**  
**GB-A- 2 152 079**  
**US-A- 3 723 165**

**NASA TECH BRIEFS, October 1988, WASH-  
INGTON, US, page 908; H.E. SLINEY ET AL:  
"LUBRIFICATION AND WEAR OF HOT CE-  
RAMICS"**

**PATENT ABSTRACTS OF JAPAN, vol. 9, no.  
91 (C-277)19 April 1985; & JP-A-59 222 566**

(73) Proprietor: **SULZER PLASMA TECHNIK, INC.**  
**1972 Meijer Drive**  
**Troy,**  
**Michigan 48176 (US)**

(72) Inventor: **Rangaswamy, Subramaniam**  
**642 Shellbourne Drive**  
**Rochester Hills,**  
**Michigan 48309 (US)**  
Inventor: **Miller, Robert Alvin**  
**14110 Balfour Avenue**  
**Oak Park,**  
**Michigan (US)**

(74) Representative: **W.P. Thompson & Co.**  
**Coopers Building,**  
**Church Street**  
**Liverpool L1 3AB (GB)**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).



## Description

The present invention relates to thermal spray powders and the use thereof in composite abradable coatings which are fabricated using thermal spray processes. More specifically, it relates to thermal spray powders of the type having a solid lubricant component and composite abradable coatings therefrom.

Materials which abrade readily in a controlled fashion are used in a number of applications, including as abradable seals. As will be appreciated by those skilled in the art, contact between a rotating part and a fixed abradable seal causes the abradable material to erode in a configuration which closely mates with and conforms to the moving part at the region of contact. In other words, the moving part wears away a portion of the abradable seal so that the seal takes on a geometry which precisely fits the moving part, that is, a close clearance gap. This effectively forms a seal having an extremely close tolerance.

One particular application of abradable seals is their use in axial flow gas turbines. The rotating compressor or rotor of an axial flow gas turbine consists of a plurality of blades attached to a shaft which is mounted in a shroud. In operation, the shaft and blades rotate inside the shroud. The inner surface of the turbine shroud is most preferably coated with an abradable material. The initial placement of the shaft and blade assembly in the shroud is such that the blade tips are as close as possible to the abradable coating.

As will be appreciated by those skilled in the art, it is important to reduce back flow in axial flow gas turbines to maximise turbine efficiency. This is achieved by minimising the clearance between the blade tips and the inner wall of the shroud. As the turbine blades rotate, however, they expand somewhat due to the heat which is generated. The tips of the rotating blades then contact the abradable material and carve precisely defined grooves in the coating without contacting the shroud itself. It will be understood that these grooves provide the exact clearance necessary to permit the blades to rotate at elevated temperatures and thus provide an effectively custom-fitted seal for the turbine.

In other gas turbines, the initial clearance is somewhat greater and the abradable coating is intended to protect the shroud and blade tips against wear during transient conditions (e.g., power surges).

In order for the turbine blades to cut grooves in the abradable coating, the material from which the coating is formed must abrade relatively easily without wearing down the blade tips. This requires a careful balance of materials in the coatings. In this environment, an abradable coating must also exhibit good resistance against particle erosion and other degradation at elevated temperatures. As known by those skilled in the art, however, these desirable characteristics have been difficult to obtain.

A number of abradable coatings have been proposed by others. These include cellular or porous metallic structures, such as illustrated in US-A- 3 689 971, US-A- 4 063 743, US-A- 4 526 509, US-A- 4 652 209, US-A- 4 664 973 and US-A- 4 671 735. Low melting point metallic coatings of indium, tin, cadmium, lead, zinc, and aluminium alloys have been suggested for use in providing "ablative" seals wherein heat generated by friction melts a clearance gap in the coating. This approach is exemplified in US-A- 2 742 224 and US-A- 3 836 156. Still others have proposed the use of hard ceramics such as  $ZrO_2$  and  $MgO$  for use in forming abradable coatings as shown in US-A- 4 405 284, US-A- 4 460 311 and US-A- 4 669 955.

In US-A- 3 508 955 a composite material is disclosed which comprises a porous metal impregnated with a fluoride of metals selected from Groups I and II of the Periodic Table of Elements. The use of fluoride salts and a barium fluoride - calcium fluoride eutectic is specifically mentioned as is the use of the material in bearings and seals. It is also disclosed therein that the resultant material can be sprayed with a surface layer of fluoride eutectic slurry which is then dried and sintered.

In US-A- 4 867 639, abradable coatings for use in turbine or compressor shrouds are disclosed which are described as low melting fluoride compounds such as  $BaF_2$ ,  $CaF_2$  and  $MgF_2$  incorporated into a higher melting temperature ceramic or metallic matrix. It is disclosed that, alternatively, the soft ceramic phase may be used to fill or impregnate a honeycomb shroud lining made of the higher melting temperature hard ceramic or metal alloy, so that the soft ceramic is not eroded by hot gases in the turbine. Zirconia and/or alumina are disclosed as the preferred high melting temperature ceramic, and NiCr and NiCrAl are disclosed as preferred metals.

The use of metal matrix coatings having a plastic component such as a polyimide are also known for use in forming an abradable seal in high-efficiency compressors. Due to the lower temperatures generated in the compressor and the fact that the rotating blades are generally softer than those found in the turbine section, plastics have been used in lieu of solid lubricants such as  $CaF_2$ . While the lower melting point of plastics is advantageous in such low temperature applications, the use of these coatings often results in the accumulation of residue on the rotating blades as well as a gradual increase in the gap between the blade and the coating because of thermal effects.

Therefore, it would be desirable to provide a composite material which abrades readily without producing significant wear of rotating parts. It would also be desirable to provide such a material which can



be fabricated using conventional thermal spray techniques. It would still further be desirable to provide such a coating which could be used to form abradable seals in relatively low-temperature environments wherein the seal material does not adhere to rotating parts. It would still further be desirable to provide a coating for forming abradable seals which can be custom formulated for a particular operating environment.

5 The present invention achieves these goals by providing thermal spray powders and composite coatings made with these powders which contain a matrix component, a solid lubricant component and a plastic component.

According to the present invention there is provided a thermal spray powder which comprises a matrix-forming component, a solid lubricant and a plastic.

10 The present invention also provides an abradable material which comprises

(a) a substantially continuous matrix, the matrix being formed of a material selected from metals, metal alloys and ceramics,

(b) solid lubricant inclusions dispersed throughout the matrix, and

(c) plastic inclusions dispersed throughout the matrix.

15 Thus, in one aspect, the present invention provides thermal spray powders which have at least three components, namely: a matrix-forming material which is preferably a metal, a metal alloy, or a ceramic material; a solid lubricant which is preferably more lubricious than the matrix-forming components; and a plastic. In one preferred embodiment, the thermal spray powders of the present invention are agglomerated particles comprising a central mass of plastic on which the matrix-forming and solid lubricant components are attached.

20 Also, in another aspect, the present invention provides abradable materials, particularly abradable coatings, having a matrix portion in which a solid lubricant and a plastic are embedded. The matrix preferably comprises either a metal, a metal alloy, or a ceramic. The solid lubricant is preferably a ceramic compound such as, for example,  $\text{CaF}_2$ , which is more lubricious than the matrix material. The plastic component is most preferably a polyimide. Numerous conventional thermal spray techniques can be used to form the coatings of the present invention.

In one embodiment, the present invention provides thermal spray powders for use in forming abradable materials such as, for example, coatings for turbine shrouds, compressor housings and other applications in which it is necessary to form an abradable seal. The thermal spray powders of the invention may be considered to be characterised by the incorporation of three components comprising: a first material which forms a matrix or quasi-continuous phase; a second material which serves as a solid lubricant in the final coating; and a third material which is a plastic. As will be described more fully herein, the combination of a solid lubricant and a plastic distributed in a matrix provides a synergistic result which in abradable coatings have unexpected superior characteristics over prior art materials.

30 The first component, i.e., the material which forms a matrix for the other materials, is selected from the group consisting of metals, metal alloys, and ceramics. As used herein "ceramic" shall be defined so as to include compounds of metallic and non-metallic elements.

Preferred metals for use as the matrix-forming component of the present invention may be selected from aluminium, titanium, copper, zinc, nickel, chromium, iron, cobalt and silicon. Alloys of these metals are also preferred for use as the first component of the present invention. Where the first component is a metal or a metal alloy, it preferably comprises from about 10 to about 90 percent by weight, more preferably from about 20 to about 70 percent by weight and most preferably from 30 to about 50 percent by weight of the thermal spray powder.

Preferred ceramics for use as the matrix-forming component of the present invention may be selected from alumina, titania, fully or partially stabilised zirconia, multicomponent oxides, including titanates, silicates, phosphates, spinels, perovskites, machinable ceramics (e.g. Corning Macor<sup>TM</sup>) and combinations thereof. Where the first component is a ceramic, it preferably comprises from about 5 to about 90 percent by weight, more preferably from about 20 to about 70 percent by weight and most preferably from about 20 to about 40 percent by weight of the thermal spray powder.

50 Preferred solid lubricants for use as the second component of the present invention are ceramics, such as, for example, ceramic fluorides, sulphides and oxides, particularly  $\text{CaF}_2$ ,  $\text{MgF}_2$ ,  $\text{MoS}_2$ ,  $\text{BaF}_2$ , and fluoride eutectics such as, for example,  $\text{BaF}_2/\text{CaF}_2$ . Other solid lubricants such as, for example, hexagonal BN may also be suitable for use in the present invention. The solid lubricant ceramic preferably comprises from about 1 to about 50 percent by weight, more preferably from about 1 to about 40 percent by weight and most preferably from about 1 to about 20 percent by weight of the thermal spray powder.

Preferred plastics for use as the third component of the present invention are thermoplastics, although it is anticipated that thermosetting plastics may be suitable in some applications. Plastics suitable for use in the present invention should desirably not become brittle at service temperatures and should desirably not



abrade rotating surfaces which contact the final coating. The preferred plastics should withstand temperatures at least up to 121 °C (250 °F) without changes. It is believed that a broad range of molecular weights will be suitable. It is estimated that the weight average molecular weight of suitable plastics may range from approximately 500 to 1,000,000, although other values may also be suitable in some instances. The molecular weight should provide the desired functional characteristics of the plastic component.

The preferred plastics are polyimides such as those described in US-A- 3 238 181, US-A- 3 426 098 and US-A- 3 382 203, most preferably thermoplastic polyimides, polyamide-imides, polyetherimides, bismaleimides, fluoroplastics such as, for example, PTFE, FEP, and PFA, ketone-based resins, also polyphenylene sulphide, polybenzimidazole aromatic polyesters, and liquid crystal polymers. Most preferred are imidized aromatic polyimide polymers and p-oxybenzoyl homopolyester such as disclosed in US-A-3 829 406 and poly(para-oxybenzoylmethyl) ester. Torlon <sup>TM</sup> and EKONOL <sup>TM</sup> are also preferred.

In some instances, graphite may be substituted for a portion of the plastic component in the present invention. With respect to the thermal spray powders of the present invention, a plastic preferably comprises from about 5 to about 90 percent by weight, more preferably from about 20 to about 70 percent by weight and most preferably from about 30 to about 50 percent by weight of the thermal spray powder.

Although the most preferred thermal spray powders of the present invention are provided as agglomerates of the three materials, i.e., matrix-forming component, solid lubricant and plastic, alternatively, the powders of the present invention may comprise blends of discrete particles of each of the three components. In this alternative embodiment, segregation in storage and during spraying as well as differential vaporization or oxidation of the components may produce less desirable coatings. Where the components are provided as blends of discrete particles, the matrix-forming component has an average particle size of from about 5 µm to about 125 µm if metallic, with the particles ranging in size from about 1 µm to about 150 µm; and from about 5 µm to about 125 µm if ceramic, with the particle size ranging from about 1 µm to about 150 µm. The solid lubricant has an average particle size of from about 1 µm to about 125 µm, with the particle size ranging up to about 150 µm; and the plastic has an average particle size of from about 5 µm to about 125 µm, with the particle size ranging from about 1 µm to about 150 µm.

The present invention will now be more fully explained in the following description of a preferred embodiment of the invention with reference to the accompanying drawings, wherein:

Figure 1 illustrates an agglomerated thermal spray particle in accordance with the present invention;

Figure 2 is a diagrammatic cross section of an abradable coating made in accordance with the present invention; and

Figures 3 to 5 are photomicrographs of an abradable coating made in accordance with the present invention.

The preferred agglomerates of the present invention are best described with reference to Figure 1 of the drawings. Accordingly, agglomerate 20 is shown having particles of a first component 22, for example, an aluminium-silicon alloy, and a second component 24, i.e., a solid lubricant such as, for example, CaF<sub>2</sub>, embedded in the surface of a third component 26 such as, for example, a polyimide. The first component serves, as previously described, as the matrix-forming component, while the solid lubricant and plastic render the coatings abradable. As previously discussed, the first component of the agglomerate may be a metal, metal alloy or ceramic material; the second component is a solid lubricant, the first and second components being embedded in or attached to the surface of the third component, i.e., a plastic.

The first component preferably comprises from about 5 to about 90 percent by weight; more preferably from about 20 to about 70 percent by weight; and most preferably from about 30 to about 50 percent by weight of agglomerate 20. The second component preferably comprises from about 1 to about 50 percent by weight; more preferably from about 1 to about 40 percent by weight; and most preferably from about 1 to about 20 percent by weight of agglomerate 20. The third component preferably comprises from about 5 to about 90 percent by weight; more preferably from about 20 to about 70 percent by weight; and most preferably from about 30 to about 50 percent by weight of agglomerate 20.

A number of methods of forming agglomerate 20 are suitable for use; however, particularly preferred is the mechanical fusion or agglomeration process set forth in EP-A- 0487272.

Accordingly, the three components (matrix-forming constituent, solid lubricant and plastic) are placed in a rotatable drum in which at least one treatment member is suspended. The drum may be generally cylindrical, having a continuous curved inner wall. The treatment member has an impact surface which is positioned adjacent the continuous curved portion of the drum. The materials are processed in the chamber by being centrifugally forced against the continuous curved surface of the chamber, whereupon the materials move between the impact surfaces of the treating members and the continuous wall surface. Forces of shear and compression are thereby exerted on the materials, causing the materials to agglomerate. This effect can be enhanced by external heating (e.g. by a hot air gun). The resultant binder-free



agglomerated particles are a composite of the three materials. In one embodiment, the treating member is rotated along the same direction as the rotation of the rotating chamber. Alternatively, the drum may be stationary with the treatment members rotating in the chamber to provide a similar result. The process parameters suitable for use in forming the thermal spray powders by this process are set forth more fully in the aforementioned co-pending European Patent Application. It may also be desirable to form the agglomerates of the present invention by conventional agglomeration techniques such as through the use of an inorganic or organic binder.

In both of the above methods, the starting materials will generally be provided in the following size ranges: metal or metal alloy as the matrix-forming component - average particle size from about 5  $\mu\text{m}$  to about 125  $\mu\text{m}$ , with particles ranging in size from 1  $\mu\text{m}$  to about 150  $\mu\text{m}$ ; ceramic as the matrix-forming component - average particle size from about 5  $\mu\text{m}$  to about 125  $\mu\text{m}$ , with particles ranging in size from about 1  $\mu\text{m}$  to about 150  $\mu\text{m}$ ; solid lubricant - average particle size from about 1  $\mu\text{m}$  to about 125  $\mu\text{m}$ , with particle size up to about 150  $\mu\text{m}$ ; and plastic - average particle size from about 5  $\mu\text{m}$  to about 125  $\mu\text{m}$ , with particles ranging in size from about 1  $\mu\text{m}$  to about 150  $\mu\text{m}$ .

In still another embodiment, the present invention provides a method of forming an abradable coating and novel coatings fabricated using the thermal spray powders disclosed herein. With reference now to Figure 2 of the drawings, coating 30 is shown deposited on substrate 32 which may comprise the inner wall of a compressor housing or the like. Coating 30 includes a matrix 34 formed of one of the above-mentioned preferred matrix-forming components such as, for example, an alloy of aluminium and silicon. Embedded in matrix 34, inclusions of one or more of the preferred plastics 36, such as, for example, a polyimide, are shown. Also embedded in matrix 34 are solid lubricant inclusions 38, for example  $\text{CaF}_2$  particles. It is to be understood that matrix 34 is a quasi-continuous phase while plastic 36 and solid lubricant 38 are generally dispersed within matrix 34 as discrete particles or bodies.

A number of thermal spray devices and techniques can be used to form the abradable coatings of the present invention, including the apparatus and process disclosed in our European Patent Applications 89309077.9 (EP-A-0361709) and 89309078.7 (EP-A-0361710).

By way of illustration only, a thermal spray powder having the characteristics described in connection with Figure 1 of the drawings in which the matrix is  $\text{AlSi}$ , the solid lubricant is  $\text{CaF}_2$  and the plastic is polyimide, is preferably thermal sprayed at a feed rate of about 20 to 70 g/min. Each agglomerate is preferably 20 to 50 percent by weight matrix-forming component; 1 to 20 percent by weight solid lubricant; and about 30 to 50 percent by weight plastic. The particles are sprayed using parameters suitable for the specific spray system. Parameters for the Plasma Technik F4 System <sup>TM</sup>, for our powder are shown in the following Table I.

TABLE I

Gun	F4	F4
Plasma Gases	Argon-Hydrogen	Helium-Argon
Nozzle	6mm (Std)	6mm (Std)
Powder Injector		
Size	2mm	2mm
Gauge	6mm	6mm
Angle	105 degrees	105 degrees
Disc (rpm)	75*	75*
Stirrer (rpm)	80	80
Spreader Assembly	SPL	SPL
Gases:	Pressure (bar)	Flow ( $\text{l}/\text{m}$ )
Primary	3.0	70 Ar
Secondary	3.0	8 $\text{H}_2$
Carrier	3.0	4.5 Ar
Current (Amps)	450	450
Voltage (V)	approx. 67	approx. 50
Spray rate **	(4.5-5) 2.04-2.27 kg/hour	2.04-2.27 kg/hour (4.5-5)
Spray distance	(4) 102mm	89mm (3.5)
(mm - the figure in parenthesis are in inches)		
* As a starting point, adjust to indicated spray rate		
** (kg/h - the figure in parenthesis are in lbs/h)		

It will be recognised that the morphology and composition of the particles, whether agglomerates or discrete particles, can change during the spray process because of thermal and kinetic effects. The solid lubricant inclusions in the final coating will typically be substantially smaller than the plastic inclusions, for example, having an average diameter of up to 50  $\mu\text{m}$ . The plastic inclusion will typically have an average



diameter of from about 5 to 124  $\mu\text{m}$ . Both the solid lubricant and the plastic will be generally uniformly dispersed in the matrix. The relative proportions of the three components in the coating will generally fall within the preferred ranges set forth with respect to the portions of the materials in the agglomerates.

The spray parameters are not generally critical, but must be compatible with the characteristics of the thermal spray powders as well as sufficient to provide a final coating as described herein. Thus, the temperature and velocity should allow the matrix-forming component to fuse, forming a matrix. The conditions should be such that neither the plastic component nor the solid lubricant substantially thermally degrade or vaporize during spraying. The solid lubricant and plastic should also not segregate in the matrix, i.e., they should be generally randomly dispersed in the matrix. In use, the coatings of the present invention most preferably serve as abradable seals in turbine and compressor housings, although numerous other applications will be apparent to those skilled in the art. It may also be desirable to form near-net shape articles using the thermal spray powders of the present invention. It may also be desirable to intentionally oxidize or vaporize the plastic component prior to provide a more porous structure.

In some instances, it may be advantageous for the plastic component of the coating to be removed by thermal treatment prior to service or by thermal exposure in service, leaving a matrix phase containing uniformly distributed pores and solid lubricant inclusions.

A number of specific coatings (and thermal spray powders used to form the coatings) are provided by the present invention which are deemed particularly useful in forming abradable coatings. More specifically, the combinations shown in Table II are particularly preferred (all percents by weight of powder, excluding binder material)

TABLE II

Matrix-forming Component	Solid Lubricant	Plastic*
AlSi 45%	CaF <sub>2</sub> 10%	Polyimide 45%
CuAl 70%	CaF <sub>2</sub> 5%	Polyimide 25%
CuNi 70%	CaF <sub>2</sub> 5%	Polyimide 25%
Ni Alloy 70%	CaF <sub>2</sub> 5%	Polyimide 25%
Fe Alloy 70%	CaF <sub>2</sub> 5%	Polyimide 25%
Co Alloy 65%	MoS <sub>2</sub> 10%	Polyimide 25%
Co Alloy 65%	BN 10%	Polyimide 25%
CuNi Alloy 70%	BaF <sub>2</sub> -CaF <sub>2</sub> 5%	Polyimide 25%

\* May substitute aromatic polyester for all or part of polyimide

The present invention will now be further described with reference to, but in no manner limited to, the following Example.

#### EXAMPLE

1,000 grams polyimide powder (-140/+325 mesh), 1,000 grams of AlSi alloy (12% by weight Si) powder (-270 mesh) and 220 grams of CaF<sub>2</sub> powder (approximately 2  $\mu\text{m}$ ) were added to a solvent blend containing 135 grams of organic binder. The ingredients were mixed at a temperature of about 149°C (300°F) until dry. The resulting agglomerates were removed and screened to yield a -70 mesh powder. The powder was plasma sprayed to form coatings on a low carbon steel substrate. Figures 3 to 5 are scanning electron photo micrographs of the resultant coatings. More specifically, in Figure 3 large (mostly 44 to 105  $\mu\text{m}$ ) inclusions of polyimide are seen embedded in an AlSi matrix. In Figures 4 and 5, the coating has been subjected to radiation causing the CaF<sub>2</sub> particles to appear as bright dots, illustrating the presence of CaF<sub>2</sub> particles throughout the matrix. It will be noted that CaF<sub>2</sub> also attaches to the plastic bodies to some extent. The coatings were found to abrade readily.

#### Claims

1. A thermal spray powder which comprises a matrix-forming component, a solid lubricant and a plastic.
2. A powder according to claim 1, wherein the matrix-forming component is selected from metals and metal-alloys.



3. A powder according to claim 1 or 2, wherein the metal or metal alloy is selected from aluminium, titanium, copper, zinc, nickel, chromium, iron, cobalt, silicon, and alloys thereof.
4. A powder according to claim 1, wherein the matrix-forming component is a ceramic.
5. A powder according to claim 4, wherein the ceramic matrix-forming component is selected from (a) oxides of aluminium, titanium, zirconium (fully or partially stabilised zirconium oxide), silicon and combinations thereof, (b) a phosphate, (c) a spinel, (d) a parovskite, (e) a machinable ceramic.
6. A powder according to any of claims 1 to 5, wherein the solid lubricant is a ceramic.
7. A powder according to claim 6, wherein the ceramic solid lubricant is selected from (a) a fluoride, (b) a sulphide, (c) an oxide, (d) boron nitride.
8. A powder according to claim 7, wherein the ceramic solid lubricant is (a) a fluoride selected from  $\text{CaF}_2$ ,  $\text{MgF}_2$ ,  $\text{BaF}_2$  and combinations thereof, (b) a fluoride eutectic, (c) a sulphide which is  $\text{MoS}_2$ .
9. A powder according to any of claims 1 to 8, wherein the plastic is thermoplastic.
10. A powder according to any of claims 1 to 8, wherein the plastic is a thermoset.
11. A powder according to any of claims 1 to 8, (b) a polyimide-imide, (c) a polyether-imide, (d) a bismaleimide, (e) a fluoroplastic, (f) a ketone-based resin, (g) a polyester, (h) a liquid crystal polymer.
12. A powder according to claim 11, wherein the plastic is selected from (a) a thermoplastic polyimide, (b) a fluoroplastic selected from PTFE, FET and PFA.
13. A powder according to any of claims 1 to 12, wherein there is, based on the weight of the thermal spray powder
  - (a) about 5 to about 90 percent by weight of the matrix-forming component, and/or
  - (b) about 1 to about 50 percent by weight of the solid lubricant, and/or
  - (c) about 5 to about 90 percent by weight of the plastic.
14. A powder according to any of claims 1 to 13, wherein the powder includes agglomerated particles containing the matrix-forming component, the solid lubricant and the plastic.
15. A powder according to claim 14, wherein the agglomerated particles are spray dried agglomerates or mechanically fused agglomerates.
16. A method of forming a thermal spray powder which comprises the steps of
  - (1) combining (a) a matrix-forming component, (b) a solid lubricant and (c) a plastic, (a) and/or (b) and/or (c) being as defined in any of claims 1 to 13, and
  - (2) agglomerating the matrix-forming component, the solid lubricant and the plastic together to form agglomerated particles.
17. A method according to claim 16, wherein there is also a step of combining a binder with the matrix-forming component, the solid lubricant and the plastic in a slurry, and wherein the agglomerating step (2) is spray-dried agglomeration.
18. A method according to claim 16, wherein the agglomerating step (2) is mechanical agglomeration.
19. An abradable material which comprises
  - (a) a substantially continuous matrix, the matrix being formed of a material selected from metals, metal alloys and ceramics,
  - (b) solid lubricant inclusions dispersed throughout the matrix, and
  - (c) plastic inclusions dispersed throughout the matrix.



20. An abratable material according to claim 19, wherein the abratable material is a coating on a substrate.
21. An abratable material according to claim 20, wherein the coating is an abratable seal, and the substrate is an engine shroud or a compression housing.
22. An abratable material according to any of claims 19 to 21, wherein the matrix-forming material, and/or the solid lubricant, and/or the plastic is or are as defined in any of claims 3 and 5 to 13.
23. A method of forming an abratable coating which comprises the steps of  
 (1) providing a powder having a matrix-forming component, a solid lubricant and a plastic, and being as defined in any of claims 1 to 15,  
 (2) heating and accelerating the powder towards a substrate with a thermal gun to form a deposit on the substrate, and  
 (3) allowing the deposit to cool on the substrate to form an abratable coating.
24. A method according to claim 23, wherein the thermal spray gun is a flame spray gun or a plasma spray gun.
25. A method according to claim 23 or 24, wherein there is also a step of removing the plastic from the abratable coating by thermal means to provide a porous abratable coating.
26. A modification of any of claims 1 to 25 wherein some of the plastic is substituted by graphite.

#### Patentansprüche

1. Thermisches Sprühpulver, welches eine matrixbildende Komponente, ein Trockenschmiermittel und einen Kunststoff umfaßt.
2. Pulver nach Anspruch 1, worin die matrixbildende Komponente unter Metallen und Metallegierungen ausgewählt wird.
3. Pulver nach Anspruch 1 oder 2, worin das Metall oder die Metallegierung unter Aluminium, Titan, Kupfer, Zink, Nickel, Chrom, Eisen, Kobalt, Silizium und Legierungen davon ausgewählt wird.
4. Pulver nach Anspruch 1, worin die matrixbildende Komponente ein keramischer Werkstoff ist.
5. Pulver nach Anspruch 4, worin die keramische matrixbildende Komponente unter (a) Oxiden von Aluminium, Titan, Zirkonium (vollkommen oder teilweise stabilisiertem Zirkoniumoxid), Silizium und Kombinationen davon, (b) einem Phosphat, (c) einem Spinell, (d) einem Perowskit, (e) einem bearbeitbaren keramischen Werkstoff ausgewählt wird.
6. Pulver nach einem der Ansprüche 1 bis 5, worin das Trockenschmiermittel ein keramischer Werkstoff ist.
7. Pulver nach Anspruch 6, worin das keramische Trockenschmiermittel unter (a) einem Fluorid, (b) einem Sulfid, (c) einem Oxid, (d) Bornitrid ausgewählt wird.
8. Pulver nach Anspruch 7, worin das keramische Trockenschmiermittel (a) ein unter  $\text{CaF}_2$ ,  $\text{MgF}_2$ ,  $\text{BaF}_2$  und Kombinationen davon ausgewähltes Fluorid, (b) ein Fluorid-Eutektikum, (c) ein Sulfid, wobei es sich um  $\text{MoS}_2$  handelt, ist.
9. Pulver nach einem der Ansprüche 1 bis 8, worin der Kunststoff thermoplastisch ist.
10. Pulver nach einem der Ansprüche 1 bis 8, worin der Kunststoff ein Duroplast ist.
11. Pulver nach einem der Ansprüche 1 bis 8, worin der Kunststoff unter (a) einem Polyimid, (b) einem Polyimid-Imid, (c) einem Polyether-Imid, (d) einem Bismaleinimid, (e) einem Fluorplast, (f) einem auf



Keton basierenden Harz, (g) einem Polyester, (h) einem flüssigen kristallinen Polymer ausgewählt wird.

12. Pulver nach Anspruch 11, worin der Kunststoff unter (a) einem thermoplastischen Polyimid, (b) einem unter PTFE, FET und PFA ausgewählten Fluorplast ausgewählt wird.
- 5 13. Pulver nach einem der Ansprüche 1 bis 12, worin bezogen auf das Gewicht des thermischen Sprühpulvers
  - (a) circa 5 bis circa 90 Gew.-% der matrixbildenden Komponente und/oder
  - (b) circa 1 bis circa 50 Gew.-% des Trockenschmiermittels und/oder
  - 10 (c) circa 5 bis circa 90 Gew.-% des Kunststoffs vorliegen.
14. Pulver nach einem der Ansprüche 1 bis 13, worin das Pulver agglomerierte Partikel einschließt, welche die matrixbildende Komponente, das Trockenschmiermittel und den Kunststoff enthalten.
- 15 15. Pulver nach Anspruch 14, worin die agglomerierten Partikel sprühgetrocknete Agglomerate oder mechanisch geschmolzene Agglomerate sind.
16. Verfahren zum Bilden eines thermischen Sprühpulvers, das die folgenden Schritte umfaßt:
  - (1) Kombinieren (a) einer matrixbildenden Komponente, (b) eines Trockenschmiermittels und (c)
  - 20 eines Kunststoffs, worin (a) und/oder (b) und/oder (c) wie in einem der Ansprüche 1 bis 13 definiert sind und
  - (2) Agglomerieren der matrixbildenden Komponente, des Trockenschmiermittels und des Kunststoffs zusammen zur Bildung agglomerierter Partikel.
- 25 17. Verfahren nach Anspruch 16, worin auch ein Schritt zum Kombinieren eines Bindemittels mit der matrixbildenden Komponente, dem Trockenschmiermittel und dem Kunststoff in einer Aufschlämmung enthalten ist und worin der Agglomerationsschritt (2) eine sprühgetrocknete Agglomeration ist.
18. Verfahren nach Anspruch 16, worin der Agglomerationsschritt (2) eine mechanische Agglomeration ist.
- 30 19. Abreibbares Material, welches folgendes umfaßt:
  - (a) Eine im wesentlichen kontinuierliche Matrix, worin die Matrix aus einem Material gebildet wird, das unter Metallen, Metallegierungen und keramischen Werkstoffen ausgewählt wird,
  - (b) Trockenschmiermitteleinschlüsse, die in der ganzen Matrix fein verteilt sind und
  - 35 (c) Kunststoffeinschlüsse, die in der ganzen Matrix fein verteilt sind.
20. Abreibbares Material nach Anspruch 19, worin das abreibbare Material eine Beschichtung auf einem Substrat ist.
- 40 21. Abreibbares Material nach Anspruch 20, worin die Beschichtung eine abreibbare Abdichtung und das Substrat eine Motorummantelung oder ein Kompressionsgehäuse ist.
22. Abreibbares Material nach einem der Ansprüche 19 bis 21, worin das matrixbildende Material und/oder das Trockenschmiermittel und/oder der Kunststoff wie in einem der Ansprüche 3 und 5 bis 13 definiert ist oder sind.
- 45 23. Verfahren zum Bilden einer abreibbaren Beschichtung, welche die folgenden Schritte umfaßt:
  - (1) Bereitstellen eines Pulvers mit einer matrixbildenden Komponente, einem Trockenschmiermittel und einem Kunststoff und welches wie nach einem der Ansprüche 1 bis 15 definiert ist,
  - 50 (2) Erhitzen und Beschleunigung des Pulvers in Richtung eines Substrats mit einer thermischen Pistole zur Bildung einer Ablagerung auf dem Substrat und
  - (3) Abkühlenlassen der Ablagerung auf dem Substrat zur Bildung einer abreibbaren Beschichtung.
24. Verfahren nach Anspruch 23, worin die thermische Sprühpistole eine Flammensprühpistole oder eine Plasmasprühpistole ist.
- 55 25. Verfahren nach Anspruch 23 oder 24, worin auch ein Schritt zum Entfernen des Kunststoffs aus der abreibbaren Beschichtung durch thermische Mittel enthalten ist, um eine poröse abreibbare Beschich-



tung bereitzustellen.

26. Modifikation eines der Ansprüche 1 bis 25, worin ein Teil des Kunststoffs durch Graphit substituiert ist.

## 5 Revendications

1. Poudre pour pulvérisation thermique qui comporte un composant de formation de matrice, un lubrifiant solide et un plastique.
- 10 2. Poudre selon la revendication 1, dans laquelle le composant de formation de matrice est sélectionné parmi des métaux et des alliages métalliques.
3. Poudre selon la revendication 1 ou 2, dans laquelle le métal ou l'alliage métallique est sélectionné parmi l'aluminium, le titane, le cuivre, le zinc, le nickel, le chrome, le fer, le cobalt, le silicium, et des alliages de ceux-ci.
- 15 4. Poudre selon la revendication 1, dans laquelle le composant de formation de matrice est une céramique.
- 20 5. Poudre selon la revendication 4, dans lequel le composant de formation de matrice céramique est sélectionné parmi (a) l'oxyde d'aluminium, de titane, de zirconium (oxyde de zirconium complètement ou partiellement stabilisé), de silicium et des combinaisons de ceux-ci, (b) un phosphate, (c) un spinelle, (d) un parovskite\*, (e) une céramique usinable.
- 25 6. Poudre selon l'une quelconque des revendications 1 à 5, dans laquelle le lubrifiant solide est une céramique.
7. Poudre selon la revendication 6, dans laquelle le lubrifiant solide céramique est sélectionné parmi (a) un fluorure, (b) un sulfure, (c) un oxyde, (d) nitrure de bore.
- 30 8. Poudre selon la revendication 7, dans laquelle le lubrifiant solide céramique est (a) un fluorure sélectionné parmi du  $\text{CaF}_2$ ,  $\text{MgF}_2$ ,  $\text{BaF}_2$  et des combinaisons de ceux-ci, (b) un fluorure eutectique, (c) un sulfure qui soit du  $\text{MoS}_2$ .
- 35 9. Poudre selon l'une quelconque des revendications 1 à 8, dans laquelle le plastique est thermoplastique.
10. Poudre selon l'une quelconque des revendications 1 à 8, dans lequel le plastique est un plastique thermodurci.
- 40 11. Poudre selon l'une quelconque des revendications 1 à 8, dans laquelle le plastique est sélectionné parmi (a) un polyimide, (b) un polyimide-imide, (c) un polyéther-imide, (d) un bismaleimide, (e) un plastique fluoré, (f) une résine de base cétonique, (g) un polyester, (h) un polymère de cristal liquide.
- 45 12. Poudre selon la revendication 11, dans laquelle le plastique est sélectionné parmi (a) un polyimide thermoplastique, (b) un plastique fluoré sélectionné parmi du PTFE, FET et PFA.
13. Poudre selon l'une quelconque des revendications 1 à 12, dans laquelle se trouve, selon le poids de la poudre pour pulvérisation thermique:
  - 50 (a) environ 5 à environ 90 pour cent en poids du composant de formation de matrice, et/ou
  - (b) environ 1 à environ 50 pour cent en poids du lubrifiant solide, et/ou
  - (c) environ 5 à environ 90 pour cent en poids du plastique.
- 55 14. Poudre selon l'une quelconque des revendications 1 à 13, dans laquelle la poudre comporte des particules agglomérées contenant le composant de formation de matrice, le lubrifiant solide et le plastique.



15. Poudre selon la revendication 14, dans laquelle les particules agglomérées sont des agglomérés séchés par pulvérisation ou des agglomérés fondus mécaniquement.
16. Procédé de formation d'une poudre pour pulvérisation thermique qui comprend les étapes suivantes
- 5 (1) combinaison (a) d'un composant de formation de matrice, (b) d'un lubrifiant solide et (c) d'un plastique, (a) et/ou (b) et/ou (c) étant comme défini dans l'une quelconque des revendications 1 à 13, et
- (2) agglomération du composant de formation de matrice, du lubrifiant solide et du plastique ensemble pour former des particules agglomérées.
- 10 17. Procédé selon la revendication 16, dans lequel se trouve également l'étape de combinaison d'un liant avec le composant de formation de matrice, avec le lubrifiant solide et avec le plastique dans une boue, et dans lequel l'étape de l'agglomération (2) est une agglomération séchée par pulvérisation.
- 15 18. Procédé selon la revendication 16, dans lequel l'étape de l'agglomération (2) est une agglomération mécanique.
19. Matière pouvant être utilisée par abrasion qui comporte:
- 20 (a) une matrice sensiblement continue, la matrice étant formée d'une matière sélectionnée parmi des métaux, des alliages métalliques et des céramiques,
- (b) inclusions de lubrifiant solide dispersé à travers la matrice, et
- (c) inclusions de plastique dispersé à travers la matrice.
- 25 20. Matière pouvant être utilisée par abrasion selon la revendication 19, dans laquelle la matière pouvant être utilisée par abrasion est un revêtement sur un substrat.
21. Matière pouvant être utilisée par abrasion selon la revendication 20, dans laquelle le revêtement est un joint pouvant être utilisé par abrasion, et le substrat est une enveloppe de protection du moteur ou un bâti de compression.
- 30 22. Matière pouvant être utilisée par abrasion selon l'une quelconque des revendications 19 à 21, dans laquelle la matière de formation de matrice, et/ou le lubrifiant solide, et/ou le plastique est ou sont comme défini(s) dans l'une quelconque des revendications 3 et 5 à 13.
- 35 23. Procédé de formation d'un revêtement pouvant être utilisé par abrasion qui comprend les étapes suivantes:
- (1) obtention d'une poudre ayant un composant de formation de matrice, un lubrifiant solide et un plastique, et étant comme défini dans l'une quelconque des revendications 1 à 15,
- 40 (2) échauffement et accélération de la poudre vers un substrat avec pistolet thermique pour former un dépôt sur le substrat, et
- (3) laisser refroidir le dépôt sur le substrat afin qu'un revêtement pouvant être utilisé par abrasion se forme.
- 45 24. Procédé selon la revendication 23, dans lequel le pistolet de pulvérisation thermique est un pistolet de projection à flamme ou un pulvérisateur de plasma.
25. Procédé selon la revendication 23 ou 24, dans lequel se trouve également l'étape d'enlèvement du plastique du revêtement pouvant être utilisé par abrasion par des moyens thermiques pour fournir un revêtement pouvant être utilisé par abrasion et poreux.
- 50 26. Modification de n'importe quelle revendications 1 à 25 dans lesquelles une partie du plastique est substituée par du graphite.



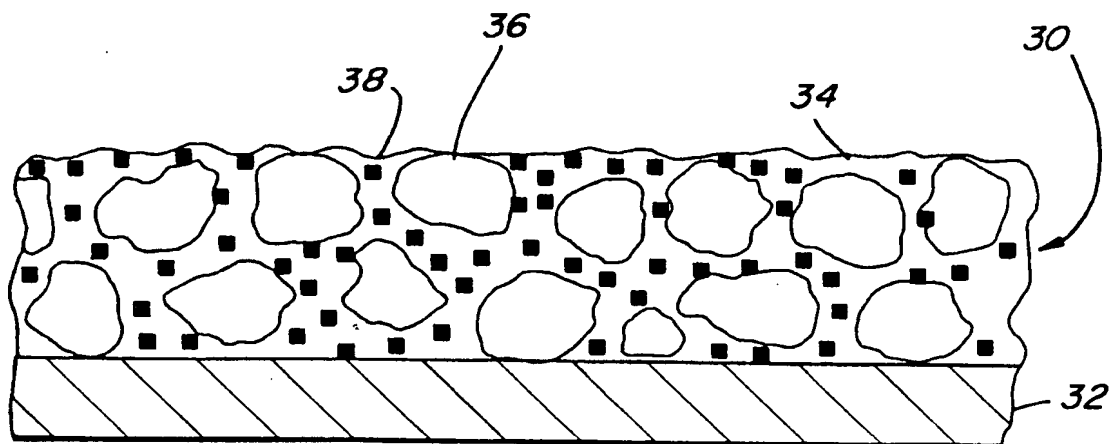
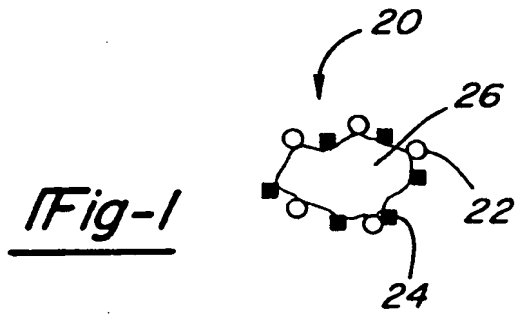


Fig-2





Fig-3



Fig-4



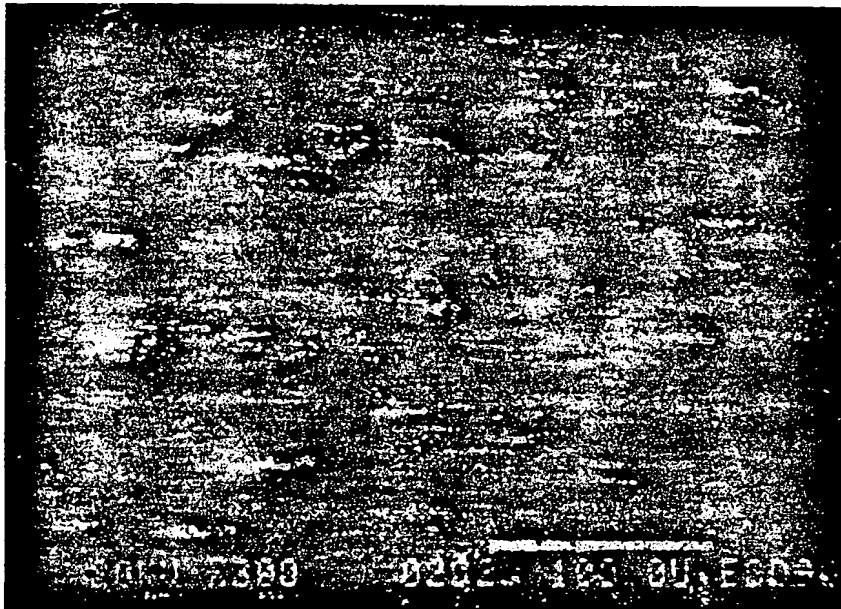


Fig-5